

Effect of Nitric Acid Concentration on the Properties of Bentonite Clay

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Bentonite is a clay mineral commonly used in various applications, particularly in wastewater treatment, due to its excellent natural adsorption properties. The objective of the present study was to investigate the effect of nitric acid activation on the composition and surface properties of bentonite clay. The bentonite was modified with different concentrations of nitric acid (1 M, 5 M, and 10 M), and the samples were characterised using X-ray fluorescence spectrometry (XRF), Brunauer-Emmett-Teller (BET), cation exchange capacity (CEC) and thermogravimetric and differential scanning calorimetry (TG-DSC) analysis. The XRF results showed that acid activation increased the amount of silicon oxide (SiO₂) while decreasing the amount of other oxides like alumina (Al₂O₃), iron oxide (Fe₂O₃), and magnesium oxide (MgO). The specific surface area, pore volume, and CEC value of the bentonite clay increased significantly as the acid concentration increased from 1 M to 10 M. The total weight loss for the samples raw bentonite (RB), activated bentonite 1 M (AB1), activated bentonite 5 M (AB5), and activated bentonite 10 M (AB10) was 79.47, 75.42, 75.20, and 74.78%, respectively.

Keywords: Bentonite; acid activation; nitric acid

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Clay minerals such as bentonite, kaolinite, and illite are fine-grained particles belonging to the hydrous aluminium silicate mineral group. These materials are naturally abundant on earth and are highly effective adsorbents, making them crucial for environmental protection. Among the various types of clays, bentonite has gained significant interest due to its large specific surface area, high pore volume, negative surface charge, and hydrophilic nature [1-2]. Bentonite is employed in several industries, including construction, oil drilling, pharmaceuticals, and most notably in wastewater treatment. It is the best candidate for adsorbing a wide range of emerging pollutants, including heavy metal ions, organic dyes, pharmaceuticals and pesticides [3-5].

Bentonite is mainly composed of montmorillonite, which is a 2:1-type phyllosilicate. It is a smectite mineral with a layered structure consisting of an aluminium octahedral sheet sandwiched between two silica tetrahedral sheets. Naturally, bentonite has a negative surface charge due to the isomorph substitution of Al³⁺ to Si⁴⁺ in the tetrahedral sheet and Mg²⁺ to Al³⁺ in the octahedral sheet [6]. In order to improve the adsorption capability of natural bentonite, various modification methods have been developed through purification, acid activation, thermal activation and a combination of thermal and acid activation [7]. Among these techniques, acid activation is the most

common method and has been extensively studied. Acid activation involves treating bentonite with acids, which can increase the surface area, pore volume, and cation exchange capacity, thereby improving its adsorption properties.

The acid activation of bentonite involves modifying it with inorganic acids like sulfuric acid (H₂SO₄) or hydrochloric acid (HCl). The acid reacts with the exchangeable cations (Al³⁺, Mg²⁺, and Fe²⁺) in the interlayer spaces of the crystal lattice, leaching out impurities and metal ions from the octahedral layer. This process weakens the bonds holding the layers together, increasing porosity and contributing to a higher specific surface area [8-9]. For instance, Selim et al. (2020) modified bentonite using sulfuric acid, which resulted in enhanced surface area and average pores volume. This modification achieved high removal efficiencies for lead and zinc of 99.67% and 99%, respectively [10]. Similarly, a study by Maged et al. (2020) found that sulfuric acid-activated bentonite significantly improved the adsorptive removal of the antibiotic ciprofloxacin, with a sorption capacity of 305.20 mg/g compared to 126.56 mg/g for natural bentonite [7]. Pawar et al. (2016) also reported that acid activation improved the surface properties of bentonite, increasing the maximum sorption capacity for copper and lead pollutants by 3.8 and 6.4 mg/g, respectively [11]. Those studies suggested bentonite modification by acid activation is particularly effective

in improving its reactivity as an adsorbent material by increasing its adsorption capacity and modifying its surface and structural properties.

Various factors must be considered during the acid activation of bentonite including the type and concentration of acid, activation time, activation temperature and the mass of bentonite. These factors play a role in enhancing the physicochemical properties of bentonite and optimizing the effectiveness of the adsorbent. This study aims to improve the surface properties of bentonite by utilising nitric acid (HNO_3) as an activation solution. As the nitric acid has not been extensively studied in prior research, the goal of this study is to investigate the effect of nitric acid concentration on the composition and surface properties of bentonite clays. To address the gap, the present study will characterise activated bentonite clays using X-ray fluorescence (XRF), cation exchange capacity (CEC) analysis, Brunauer, Emmet, and Teller (BET), thermogravimetry analysis (TG), and differential scanning calorimetry (DSC).

EXPERIMENTAL

Chemicals and Materials

The bentonite utilized in this study was supplied by Sigma Aldrich. The average particle size of the bentonite was measured to be approximately 8.25 μm . Nitric acid with concentration of 65% and specific gravity of 1.39 g/cm^3 was supplied by Merck Sdn. Bhd. The raw bentonite used in the experiment was denoted as RB and subjected to the acid activation process.

Characterization Methods

The acid activation of bentonite clay was conducted using nitric acid. 30 g of bentonite sample was added into 300 ml of the acid solution and the mixture was stirred at room temperature for four hours. Subsequently, the mixture was filtered using a Buchner funnel and the residual bentonite clay was washed using distilled water and dried in an oven at 60 $^\circ\text{C}$ for 24 hours. The activated bentonite clay was stored in airtight plastic bottles. The acid activation was carried out by varying the acid concentrations of 1, 5 and 10 M and denoted as AB1, AB5 and AB10, respectively.

Bentonite clay was characterized before (sample RB) and after acid activation (AB1, AB5 and AB10). The chemical composition of bentonite was determined by XRF using a Shimadzu XRF-1700 spectrometer. To evaluate textural properties such as surface area, total pore volume and pore size, nitrogen adsorption-desorption isotherms were measured using Anton Paar Nova 600 instrument. Prior to analysis,

the samples were degassed at 150 $^\circ\text{C}$ for 6 hours to eliminate any residual moisture. The specific surface area was determined using the BET equation at a relative pressure of 0.99, while the pore size and total pore volume were calculated using the Barrett, Joyner, and Halenda (BJH) method.

CEC measurements were conducted to assess the ion exchange capacity of the studied samples. Ammonium acetate was used as the exchange solution, allowing the ammonium ions to replace the existing cations in the bentonite structure. Subsequently, the supernatant was treated using sodium hydroxide solution to convert the ammonium ions into ammonia, which was then distilled into a known volume of acid. The resulting distillate was titrated using the Kjeldahl method to quantify the ammonium ions that presented in the sample. TG-DSC of the bentonite samples were performed using LINSEIS Simultaneous Thermal Analysis, STA PT 1600 instrument. All experiments were carried out by placing ± 30 mg of sample in an alumina crucible and heating it from room temperature to 1000 $^\circ\text{C}$ under an open-air flow, with a heating rate of 10 $^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Chemical Composition

Table 1 presents the chemical analysis of the raw bentonite and acid-activated bentonite as evaluated by XRF. According to the XRF data, the primary oxides contained in the bentonite were SiO_2 and Al_2O_3 , with trace levels of other oxides, such as Fe_2O_3 , MgO , CaO , Na_2O , K_2O , and TiO_2 . Previous work by Maged et al. (2020) has found after the acid activation, the Egypt bentonite showed a significant change in the chemical composition in the modified bentonite clay, compared to the raw bentonite clay [7]. The same observation was also reported by Krupskaya et al. (2019) [12]. Based on the current findings, the utilization of nitric acid with various concentrations ranging from 1 to 10 M resulted in the remobilization of octahedral cations from the smectite structure. This process led to an increase in SiO_2 content in all activated bentonite samples and this increase was attributed to the accumulation of amorphous silica on particle surfaces, thereby enhancing the adsorption capacity of the bentonite [9]. Additionally, the acid activation process caused the dissolution of exchangeable cations in the octahedral sheet, leading to a decrease in the content of Al_2O_3 , Fe_2O_3 , MgO , CaO , K_2O , and Na_2O as the acid concentration increased. This alteration in chemical composition may impact the overall stability and ion exchange capacity of the bentonite samples.

Table 1. Chemical composition of raw bentonite and acid-activated bentonite.

Clay sample	Chemical composition (%)										Loss on ignition (%)
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Cr ₂ O ₃	TiO ₂	K ₂ O	Na ₂ O	P ₂ O ₅	
RB	51.96	14.17	4.19	3.06	2.37	0.01	0.49	0.11	0.78	0.04	22.82
AB1	53.98	14.02	4.09	2.94	0.63	0.01	0.51	0.09	0.22	0.03	23.48
AB5	54.56	13.98	3.82	2.87	0.21	0.01	0.52	0.07	0.09	0.03	23.84
AB10	55.02	13.22	3.48	2.83	0.09	0.01	0.54	0.07	0.06	0.03	24.65

Surface Properties

In order to examine the surface properties of the raw and acid-activated bentonite, the nitrogen adsorption-desorption isotherm was obtained to determine the specific surface area and pores properties. The results were presented in Table 2, Figure 1 and Figure 2. As indicated in Table 2, the RB had a specific surface area of 32.9 m²/g. After acid activation, the specific surface area experienced a notable increase, ranging from approximately 2.7 to 3.9 times greater for the acid-activated samples as compared to the untreated sample. Specifically, the specific surface area values for AB1, AB5, and AB10 were 88.2 m²/g, 131.1 m²/g, and 128.7 m²/g, respectively. This finding indicated the pore size of the acid-activated bentonite was significantly improved as compared to raw bentonite. This could be the result of nitric acid activation, which successfully exposed the raw bentonite plate edges and increased their surface area [13].

It is evident that there was an increase in total total pore volume following acid activation. The pore volume exhibited a slight increment as the nitric acid concentration increased. As depicted in Table 2, the pore volume of the acid-activated sample increased from 0.0698 (RB) to 0.0866, 0.1018 and 0.1075 cm³/g for AB1, AB5, and AB10, respectively. This finding demonstrated that nitric acid activation successfully

leached out the impurities and octahedral cations from the bentonite structure. Consequently, it facilitated alterations in the texture properties, and leading to the formation of highly porous particles.

As shown in Figure 1, the volume of adsorbed nitrogen generally increased as the acid concentration increased across the entire range of relative pressure values. The first part of the isotherm ($p/p^0 < 0.40$) can be attributed to the monolayer-multilayer region. When the relative pressure exceeded 0.40, a hysteresis loop was observed until the relative pressure approached 0.99. This hysteresis loop indicated the presence of mesopores [14]. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, the isotherm of all samples exhibits characteristics of Type IV, with the hysteresis loop strongly associated with capillary condensation occurring in mesopores. This finding suggested the occurrence of mesoporous capillary condensation within this pressure range. Furthermore, the analysis of adsorption and desorption is also important for understanding the pore size distribution of the acid-activated sample. As presented in Figure 2, the pore size distribution curves of all samples exhibited a similar pattern. The majority of pores were identified between 3 and 4 nm in diameter, indicating that the entire surface of the bentonite was mesoporous, as observed in the isotherm curves.

Table 2. Pore properties of raw bentonite and acid-activated bentonite.

Properties	Clay samples			
	RB	AB1	AB5	AB10
Specific surface area (m ² /g)	32.92	88.27	131.15	128.71
BJH pore volume (cm ³ /g)	0.0698	0.0866	0.1018	0.1075
Average pore diameter (nm)	4.1339	3.7799	3.7715	3.7562

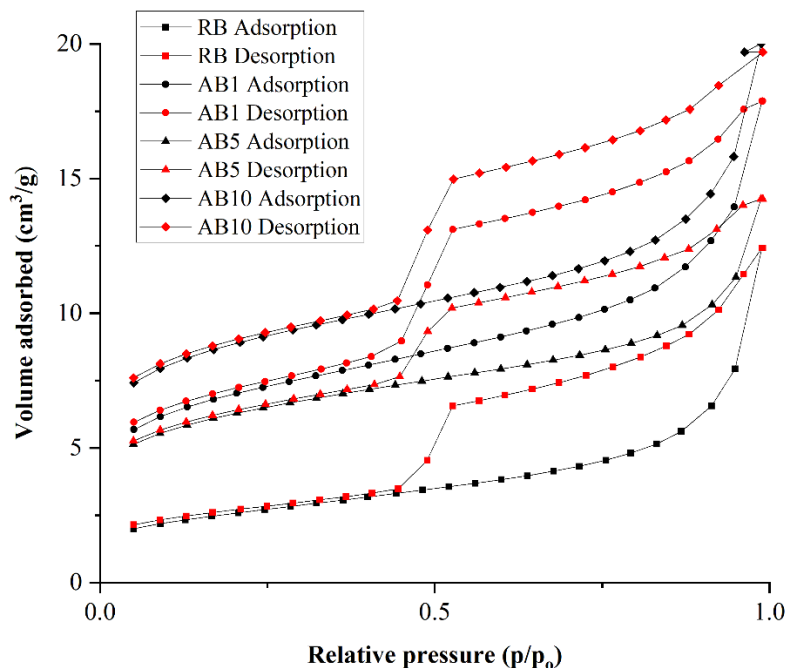


Figure 1. Nitrogen adsorption-desorption isotherm of the raw bentonite and acid-activated bentonite.

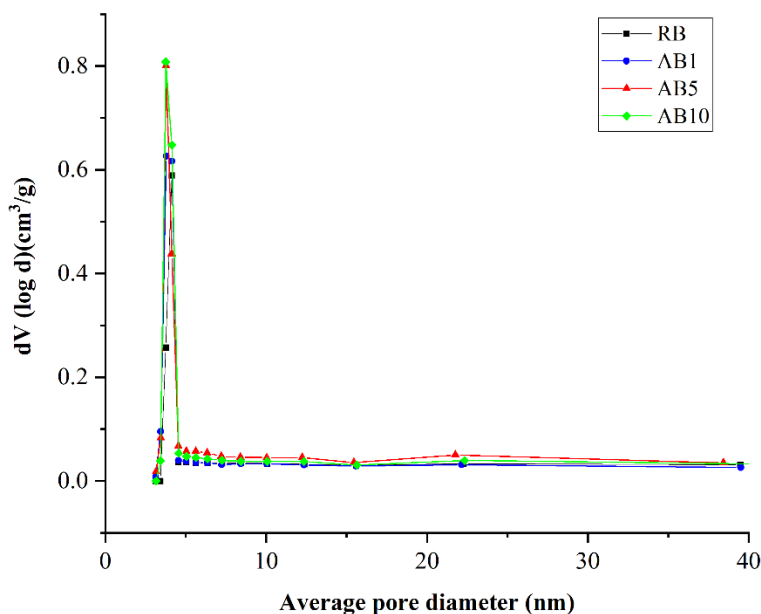


Figure 2. Pore distribution of the raw bentonite and acid-activated bentonite at different acid concentration.

Cation Exchange Capacity (CEC) Measurements

The CEC analysis is important for understanding the adsorption and ion exchange capabilities of the adsorbent materials. CEC is defined as the number of equivalents of a cation that can be adsorbed per unit weight of adsorbent. Table 3 presents the results of the CEC values for both raw and acid-activated

bentonite samples. Previous works have reported varying CEC values for raw bentonite obtained from different deposits. For instance, Mohellebi and Lakel (2015) reported a CEC of 136 meq/100g for raw bentonite from Algerian, while Nagahashi (2021) reported a value of 100.1 meq/100g. Generally, clay minerals exhibit CEC values ranging between 3 and 150 meq/100g [15, 16].

Table 3. CEC values of bentonite before and after acid activation.

Clay samples	Cation exchange capacity (meq/100g)			
	RB	AB1	AB5	AB10
	120	132	136	146

The CEC value obtained for the raw bentonite in this study was 120 meq/100g, which was in the range of CEC values reported for commercial-grade bentonite in previous study. From Table 3, it was evident that the CEC values follow the order of RB < AB1 < AB5 < AB10, indicating the exchange capability of the acid-activated bentonite increased with higher acid concentrations, ranging from 1 M to 10 M. This increase in CEC was attributed to the creation of pores during acid activation, facilitated by partial dissolution and protonation processes [17].

Thermogravimetric Analysis

Figure 3 and Table 3 displayed the TG - DSC curves of raw bentonite and acid activated bentonite conducted within the temperature ranging from 25 to 1000 °C. As depicted in Figure 3, the TG-DSC analysis of RB revealed an initial weight loss of approximately 16% occurring between 30 and 170 °C, with a corresponding endothermic peak at 116 °C, indicative of dehydration and water volatilization. A minor endothermic peak was also observed at 188 °C, likely attributed to simultaneous reaction such as water boiling. Subsequently, a second weight reduction, predominantly between 200 °C and 600 °C was observed that might be attributed to the elimination of tightly bound water species coordinated to the interlayer cations in the montmorillonite mineral [18]. Around 664°C, a slight endothermic peak is obtained, corresponding to dehydroxylation from the crystal structure in bentonite, with a corresponding weight loss of approximately 2.69%. Finally, a major endothermic peak was observed between 740 and 900 °C, with the maximum peak at

842 °C, indicating the breakdown of the internal structure of the bentonite [13].

The thermal analysis of acid-activated bentonite samples (AB1, AB5 and AB10) exhibited similar characteristics as illustrated in Figure 3. Between 30 to 180 °C, a significant weight loss was observed for all samples, attributed to the evaporation of adsorbed and interlayer water from the clay. However, as compared to the raw bentonite, it was evident that the first endothermic peak of acid-activated bentonite was shifted to a lower temperature, slightly below 100 °C. This shift is likely due to the hydrophobic nature of the activated bentonite [15]. In addition, a weight loss was also observed between 750 and 900 °C with an endothermic peak at 865 °C, 871 °C and 845 °C for AB1, AB5 and AB10, respectively. This phenomenon was attributed to the dehydroxylation of the OH structural group, leading to the disruption of the mineral structure of the bentonite.

As indicated in Table 3, RB exhibited the highest residual weight approximately 79% due to the presence of impurities and non-clay minerals, which were unable to undergo water physisorption within its structure. On the other hand, the acid activation of bentonite results in structural modifications that helped to dissolve impurities and caused an expansion of the clay mineral layers. This expansion increased surface area and enhanced the reactivity of the clay [12]. Consequently, due to these structural changes, water molecules and other volatile components were driven off during heating, leading to a higher weight loss, with residual weights approximately ranging from 74% to 75%.

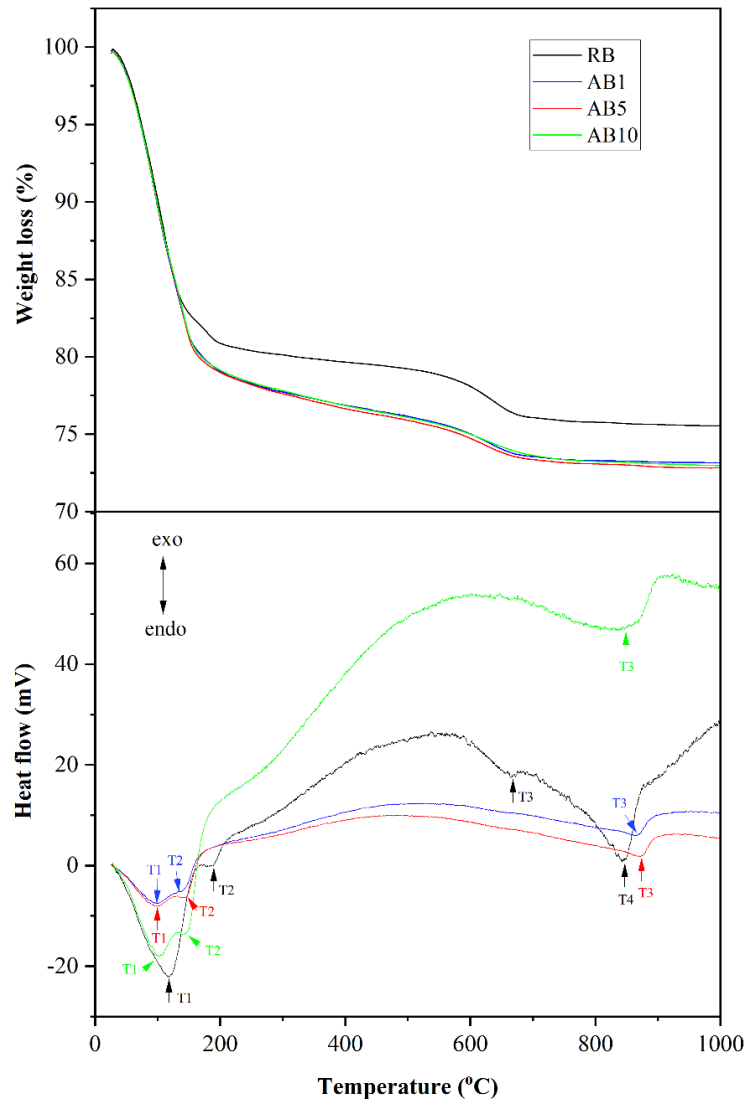


Figure 3. TG-DSC curves of raw bentonite and acid-activated bentonite.

Table 4. TG-DSC data for raw bentonite and acid-activated bentonite.

Sample	Temperature range (°C)	Peak Temperature (°C)	Weight loss (%)	Residual weight, (%)
RB	30-170	116 (T1)	16.00	79.47
	170-210	188 (T2)	1.69	
	600-720	664 (T3)	2.69	
	740-900	842 (T4)	0.15	
AB1	30-160	96.9 (T1)	17.50	75.42
	140-170	138 (T2)	4.89	
	800-900	865 (T3)	2.19	
AB5	30-140	96 (T1)	18.82	75.20
	140-180	146 (T2)	4.14	
	800-900	871(T3)	1.84	
AB10	30-140	98 (T1)	19.08	74.78
	140-180	151(T2)	5.83	
	750-900	846 (T3)	0.31	

CONCLUSION

In this study, the effect of nitric acid concentrations on the properties of bentonite clay was thoroughly investigated. The findings revealed that acid activation effectively modified the composition and surface properties of the bentonite by leaching out the octahedral cations from the clay sheet. With the increase in acid concentration from 1 M to 10 M, the composition of SiO₂ increased from 51.96% (RB) to 55.02% (AB10), while the composition of Al₂O₃, Fe₂O₃, MgO and CaO decreased. Additionally, acid activation led to an increase in the cation exchange capacity (CEC) from 120 meq/100g (RB) to 146 meq/100g (AB10). Furthermore, the results from BET analysis revealed that acid activation significantly enhanced the specific surface area and average pore volume of the bentonite. TG-DSC demonstrated a notable weight loss for both raw bentonite (RB) and acid-activated samples of AB1, AB5, and AB10 ranging from 20% to 25%. Overall, this study contributed to the existing literature by highlighting the potential use of nitric acid as an activating agent for bentonite clay and underscored the applications of activated bentonite in adsorption studies aimed at removing toxic contaminants from wastewater.

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